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# Recovery of nutrients from the liquid fraction of digestate: Use of enriched zeolite and biochar as nitrogen fertilizers

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## Abstract

The liquid fraction after liquid/solid separation of biogas digestate has a high potential as a fertilizer due to its high nutrient concentration. However, the direct application of digestate in agricultural fields results in practical problems due to its voluminous nature. One solution to this could be to concentrate nutrients onto sorbents such as biochar or zeolites, which can subsequently be used as a fertilizer. This study investigated the ability of biochar and zeolite 'clinoptilolite' enriched with digestate nutrients to supply nitrogen (N) when used as a fertilizer. A pot experiment with ryegrass was conducted to test the effect of a nutrient-enriched biochar and clinoptilolite by determining plant biomass growth and N uptake. This included untreated biochar and clinoptilolite as controls and two levels of N application (15 and 45 mg N per pot) each at two initial loading ratios (low and high). Nutrient-enriched biochar and clinoptilolite increased plant biomass yield (up to 1.02 and 2.39 g per pot) and N uptake (up to 11.23 and 39.94 mg N per pot) compared to the untreated sorbents treatments. Initial loading ratio had a significant effect on plant biomass response and apparent N recovery (ANR) for enriched clinoptilolite, and lower initial loading ratio improved plant growth. In contrast to clinoptilolite, higher initial loading ratio resulted in higher ANR. In conclusion, our results reveal that N released from enriched clinoptilolite and biochar could be taken up by the plants, clinoptilolite performed more effectively than biochar, and initial loading ratio affected the performance of the sorbents when used as a fertilizer.

**Key words:** biogas digestate / clinoptilolite / double-pot technique / enriched sorbent / initial loading / slow release N fertilizer

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## 1 Introduction

Digestate from anaerobic digestion in biogas plants shows comparable properties to animal slurry, both physically and as a fertilizer. This is the case not only when manure is the only feedstock, but also when additional organic waste feedstock is used for co-fermentation. Digestate is, therefore, often processed and managed in a similar way to animal slurry. In areas with a high animal density and, hence, a nutrient surplus compared to crop requirements, mechanical slurry separation can be used as a method to facilitate redistribution of nutrient surpluses to other areas (Møller et al., 2000; Paavola and Rintala, 2008; Jørgensen and Jensen, 2009). The solid fraction resulting from the separation contains most of the dry matter and phosphorus (Hjorth et al., 2009, 2010), but constitutes only 10–25% of the total mass, so it can be transported more easily and economically to regions with lower animal densities and no nutrient surplus (Møller et al., 2000, 2007).

The liquid fraction of separated manure and digestate, which has a high water content and low nutrient concentration, can be applied directly to agricultural land in the vicinity of the farm or the biogas plant (Hjorth et al., 2010; Fuchs and Drosig, 2013). However, in areas with very high animal densities or no cropping land suitable for digestate fertilization, environmentally friendly management and utilization of the liquid fraction presents a challenge as well as other manure-derived by-products (Zarebska et al., 2015). Transportation of large volumes of liquids is costly and ineffective (Rehl and Müller, 2011). Furthermore, environmental problems, such as gaseous emissions of malodors, ammonia, and greenhouse gases as well as nutrient runoff to streams and waterways, may occur when the liquid fraction of digestate is applied to agricultural land (Hjorth et al., 2009). To overcome such problems, recovery and concentration of nutrients from the liquid fraction may be a desirable option, and one potential method for this could be sorption to a solid carrier. Both inorganic and organic materials have been used successfully for nutrient sorption. Clinoptilolite, a natural zeolite (aluminosilicate) and a well-known cation exchanger, has been used to remove nu-

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trients from source-separated urine (Ganrot et al., 2007; Beler Baykal et al., 2009; Beler-Baykal et al., 2011; Kocatürk and Baykal, 2012; Allar and Beler Baykal, 2015). Several studies have described the sorption of ammonium and other nutrients to biochar, a carbonaceous product from the pyrolysis of biomass (Eldridge et al., 2010; Hale et al., 2013; Sarkhot et al., 2013; Gai et al., 2014; Jassal et al., 2015; Wang et al., 2015a).

A sorbent should be cost-effective in concentrating nutrients. However, if the product is to be used as a fertilizer, the nutrient-enriched sorbent should also release the nutrients in synchrony with crop demand. Clinoptilolite acts as a slow-release fertilizer when added to soil (Perrin et al., 1998; Reháková et al., 2004) since it is able to desorb nutrients following the enrichment step (Kithome et al., 1998; Ganrot et al., 2007; Hedström and Rastas Amofah, 2008; Beler-Baykal et al., 2011; Cyrus and Reddy, 2011). Biochar has also been reported to release nutrients subsequent to enrichment (Hale et al., 2013; Sarkhot et al., 2013; Hina et al., 2015; Jassal et al., 2015; Wang et al., 2015b), but only a few studies report on the performance of enriched biochar as a fertilizer (Taghizadeh-Toosi et al., 2012a, 2012b). For the practical implications of using sorbents to remove nutrients from the liquid fractions of digestate, it is important to have knowledge on the effectiveness of the enriched sorbents in terms of supplying nutrients to plants.

Initial loading ratio, *i.e.*, the ratio of the amount of nutrients to the amount of sorbents, has been described as an important design parameter for ion exchange/sorption processes, which influences the nutrient removal efficiency from the liquid fraction and consequently the degree of enrichment of nutrients on the sorbent material (Belér Baykal et al., 2009; Kocatürk-Schumacher et al., 2017a, 2017b). The effect of initial loading ratio on the plant availability of N sorbed to clinoptilolite and biochar has not been investigated when enriched clinoptilolite and biochar are used as fertilizers. This information is important when clinoptilolite and biochar are to be used both for the treatment of the liquid fraction of digestate and as fertilizers following the enrichment process.

The objectives of this study were to assess the effects of digestate nutrient-enriched clinoptilolite and biochar on plant growth by measuring biomass yield and nitrogen (N) uptake and by calculating biomass response (BR) and apparent nitrogen recovery (ANR). We hypothesized that (1) nitrogen sorbed to clinoptilolite and biochar is readily available to plants and will result in a higher biomass yield and N uptake compared to the control (untreated clinoptilolite and biochar), (2) nitrogen sorbed to clinoptilolite is as available to plants as N sorbed to biochar, and both enriched sorbents will result in similar BR and ANR at the same N application level, (3) initial loading ratio and, hence, the N enrichment of clinoptilolite and biochar do not affect plant growth, and low and high initial loading ratios will result in similar BR and ANR at the same N application level.

## 2 Material and methods

### 2.1 Experimental set-up

We used the double-pot technique (Janssen, 1990), in which plants were grown in a two-tier pot (Fig. 1). The upper compartment contained quartz sand without nutrients, to which only the material to be tested was added. The lower compartment contained a nutrient solution with all the essential nutrients except the one whose availability was quantified in the top compartment. At the bottom of the upper compartment, a mesh (1 mm pore size) allowed roots to grow through to the bottom compartment. With the double-pot technique, the optimal availability of all nutrients, except the one being tested, can be guaranteed by the nutrient solution in the lower pot (Antil et al., 2009). The difference in growth between plants is a measure of the availability of the tested nutrient in the upper compartment.

In our study, the upper pot (0.25 L with 6.8 cm diameter) was filled in two steps. In the first step, a mixture of 200 g quartz sand and the product to be tested (biochar, clinoptilolite or synthetic fertilizer, product amounts presented in Tab. 1) were added. In the second step, a germination layer was created by adding 100 g quartz sand and ryegrass (*Lolium perenne* L.) seeds, sown at 1 cm depth at a rate of 0.40 g seeds per pot. The quartz sand was inoculated with a solution containing soil micro-organisms, which was prepared by filtering a mixture of 50 g soil and 2 L deionized water through a coarse filter paper. Each upper pot was placed on a lower pot (1 L) containing a nutrient solution, from which N was omitted. The composition of the nutrient solution in the lower pots was (mM): 1 MgSO<sub>4</sub>, 0.5 KH<sub>2</sub>PO<sub>4</sub>, 1.0 K<sub>2</sub>SO<sub>4</sub>, 2.0 CaCl<sub>2</sub>, with trace elements (μM) 46.0 B, 9.1 Mn, 0.8 Zn, 0.3 Cu, 0.1 Mo, and 14.4 Fe. The nutrient solutions in the lower pots were changed once a week.

There was a small space between the upper and lower pot in order to prevent direct transport of water and nutrients between the two layers. The upper pots were watered with deionized water three times a week to keep the moisture level corresponding to approximately 60% of the water-holding ca-



Figure 1: Greenhouse experiment using double-pot technique.

**Table 1:** Overview of the treatments.

Treatment	Abbreviation	Initial loading ratio (mg NH <sub>4</sub> -N g <sup>-1</sup> )	Total N concentration of sorbent (mg N g <sup>-1</sup> )	N application (mg N per pot)	Amount of sorbent applied (g per pot)
Biochar					
Control	BCon	0	1.68	0	5.58 <sup>a</sup>
Low	BL15	10	8.07	15	1.86
	BL45			45	5.58
High	BH15	40	9.58	15	1.57
	BH45			45	4.70
Clinoptilolite					
Control	CCon	0	0.05	0	5.98 <sup>a</sup>
Low	CL15	10	7.52	15	1.99
	CL45			45	5.98
High	CH15	52	14.73	15	1.02
	CH45			45	3.05
Reference					
Control, unfertilized	SCon	n/a <sup>b</sup>	n/a	0	n/a
Synthetic N solution	S15	n/a	n/a	15	n/a
	S45			45	n/a

<sup>a</sup> The amount of untreated biochar and clinoptilolite in the control experiments was set to the same amount as that used for the low initial loading ratio (10 mg NH<sub>4</sub>-N g<sup>-1</sup>) and 45 mg N per pot application rate for biochar and clinoptilolite.

<sup>b</sup> n/a: For the control treatment and synthetic N application, initial loading ratio, N content and amount of sorbent are not applicable.

capacity of the control treatment (only sand and water). This was done by recording the initial weight of each pot (after adding the pot content) on the first day of the experiment and adding the necessary amount of water in the pot at each watering event to reach the initial weight. The pots were weighed on a scale at each watering event and deionized water was added until the initial weight of each pot was reached. Double pots were allocated at random to trays (eight pots per tray) at the beginning of the experiment, and shifted at random between trays every 7 d. The experiment was carried out in a greenhouse with four replicates at an average temperature of 17°C and an average humidity of 62%, providing 16 h of artificial light (80–100 µmol cm<sup>-2</sup> s<sup>-1</sup> light intensity) a day.

Above-ground biomass was harvested after 21, 36, and 70 d. On the last date, roots in the lower and upper pots were also harvested. Roots were separated from sand and fertilizer materials by washing with deionized water. The separated roots were dipped into 0.01 M HCl solution and rinsed again with deionized water to wash any ions away that could originate from the nutrient solution in the lower pot. Dry matter yields of above-ground biomass and roots were determined after drying the plant materials at 70°C for 72 h. Samples were ground and digested in a mixture of sulfuric acid, salicylic acid, and Se, to which H<sub>2</sub>O<sub>2</sub> was added. Total N was colorimetrically determined in the digest by a segmented flow analyzer (Terminghoff and Houba, 2004).

Biomass yield was calculated as the sum of the above-ground biomass of all three cuts *plus* the roots at the final harvest. Total N uptake was calculated as the sum of N in all cuts and roots. The root-to-mass ratio (RMR), which is an indicator of N availability, was calculated as:

$$RMR = \frac{B_r}{B_t}, \quad (1)$$

where  $B_r$  is root biomass and  $B_t$  is total biomass for each treatment. RMR is bounded between 0 and 1. Lower RMR values indicate increasing nitrogen availability due to less biomass allocation to the roots as compared to the leaves (Wilson, 1988; Poorter and Nagel, 2000; Pérez-Harguindeguy et al., 2013).

## 2.2 Treatments

Nutrient-enriched clinoptilolite and biochar were produced by sorption of nutrients from the liquid fraction of digestate in previous studies by the authors (Kocatürk-Schumacher et al., 2017a, 2017b). The clinoptilolite used was from Gördes in Turkey with a typical composition of 65–72% SiO<sub>2</sub>, 10–12% Al<sub>2</sub>O<sub>3</sub>, 0.7–1.9% Fe<sub>2</sub>O<sub>3</sub>, 0.1–0.5% Na<sub>2</sub>O, 2.5–3.8% K<sub>2</sub>O, 2.4–3.7% CaO, 0.9–1.2% MgO, 0–0.08% MnO, and 0.02–0.05% P<sub>2</sub>O<sub>5</sub> (Rota Mining Co.), which corresponds to 30.4–33.7% Si, 5.3–6.3% Al, 0.5–1.3% Fe, 0.1–0.4% Na,



2.1–3.2% K, 1.7–2.6% Ca, 0.5–0.7% Mg, 0–0.06% Mn, and 0–0.02% P. The clinoptilolite samples used in the nutrient enrichment procedure had a particle size of 1–3 mm, a pH of 8.5, with 150–210 cmol<sub>c</sub> kg<sup>-1</sup> cation exchange capacity (CEC, data provided by the manufacturer), and 35.5 m<sup>2</sup> g<sup>-1</sup> specific surface area (DIN 66132/ISO 9277). Biochar was produced from holm oak by slow pyrolysis at 650°C under no oxygen conditions and atmospheric pressure (Proinso Inc. Málaga, Spain) and had an ash content of 11.3% (dry basis), composition of 76.5% C, 1.4% H, 0.8% N, 7% O, 0.2% P, 0.6% K, 0.04% Na, 5% Ca, 0.3% Mg, 0.05% Fe, 0.14% Al, 0.2 H : C ratio, and 0.1 O : C ratio (Ross, 2016 *pers. comm.*). Biochar samples with a particle size of 1–4 mm were used in the enrichment procedure and the samples had a pH of 8.2, 42.3 cmol<sub>c</sub> kg<sup>-1</sup> CEC (Dijk, 2015), and 166 m<sup>2</sup> g<sup>-1</sup> specific surface area (DIN 66132/ISO 9277).

Sorbent materials were separately brought into contact with the liquid fraction of digestate, which resulted in the retention of nutrients on the sorbent materials as described in Kocatürk-Schumacher et al. (2017a, 2017b). The enrichment of the sorbents was done by pumping the liquid fraction of digestate through a column packed with clinoptilolite or biochar. The liquid fraction of digestate was fed into the columns by a peristaltic pump (Masterflex L/S Series) at 100% recycling in the upflow mode up to 120 h. The liquid fraction of digestate was from a full-scale biogas plant (Fangel Bioenergy ApS, Odense, Denmark) using pig slurry as the main feedstock with co-digestion of food waste. The liquid fraction was produced by a decanting centrifuge treatment of the digestate. Two initial loading ratios were applied, namely 10 (low) and 52 (high) mg NH<sub>4</sub>-N g<sup>-1</sup> for clinoptilolite, and 10 (low) and 40 (high) mg NH<sub>4</sub>-N g<sup>-1</sup> for biochar. The selection of the different initial loading ratios was made based on practical grounds due to insufficient amount of material. The closest initial loading ratios for enriched materials were used. The N concentrations of the biochar and clinoptilolite prior to and after nutrient enrichment are shown in Tab. 1.

Enriched sorbents were mixed with quartz sand at two levels, 15 and 45 mg N per pot, which corresponded to 150 and 450 kg of N per ha, respectively. A synthetic NH<sub>4</sub>NO<sub>3</sub> solution was used as a reference fertilizer and applied at the same N application levels. Sand mixed with untreated (non-enriched) biochar or clinoptilolite and pure sand (no addition of N solution, biochar or clinoptilolite) were used as controls. Untreated biochar and clinoptilolite, used for the control treatments, contained some N, which, however, was so little that it could not be extracted with 0.01 CaCl<sub>2</sub> (data not shown). The amount of untreated clinoptilolite and biochar applied in the controls was the same as the highest amount of nutrient-enriched biochar and clinoptilolite applied in the experiment.

### 2.3 Statistical analysis

We tested the effect of enriched sorbents on plant growth by analyzing biomass and total N-uptake data separately for each treatment (clinoptilolite, biochar, and synthetic solution) with one-way ANOVA tests. Each sub-treatment was compared with the corresponding control, and for each outcome (bio-

mass and N uptake) the P values were adjusted with the Holm method in order to correct for multiple testing. Biomass and N-uptake data were analyzed using linear regression on the amount of applied N, allowing for different coefficients for each treatment. The slopes of the regression models represented the biomass response (BR) and apparent N recovery (ANR) for each treatment. The effect of various N applications (enriched biochar, enriched clinoptilolite, and synthetic N solution) was tested by comparing BR and ANR for each treatment.

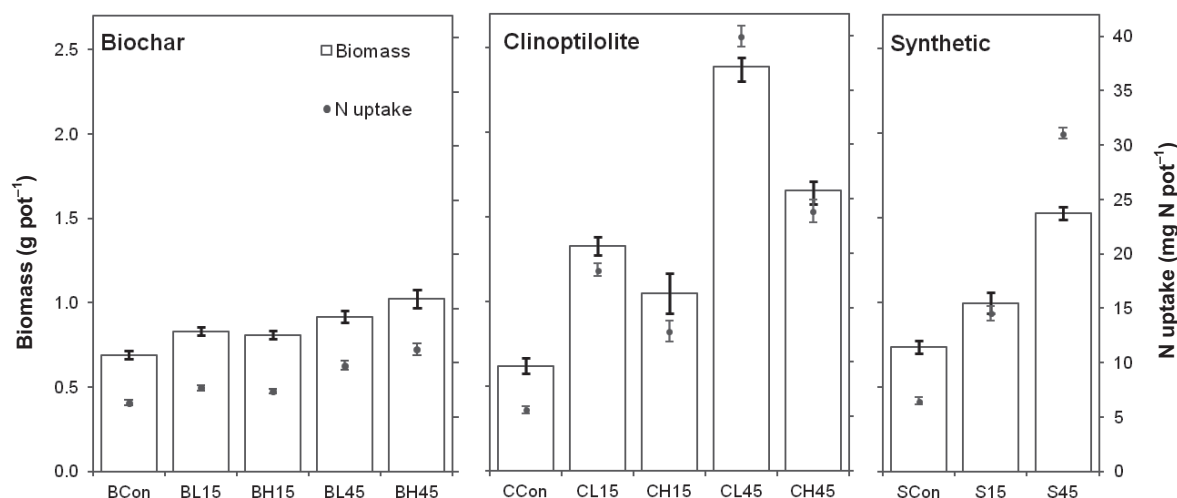
Furthermore, regression analysis was used to test for the effect of initial loading ratio of the biochar and clinoptilolite on plant availability of N by comparing BR and ANR for clinoptilolite and biochar separately. The statistical analysis was conducted using the statistical software R version 3.2.1 (R Core Team, 2015).

## 3 Results

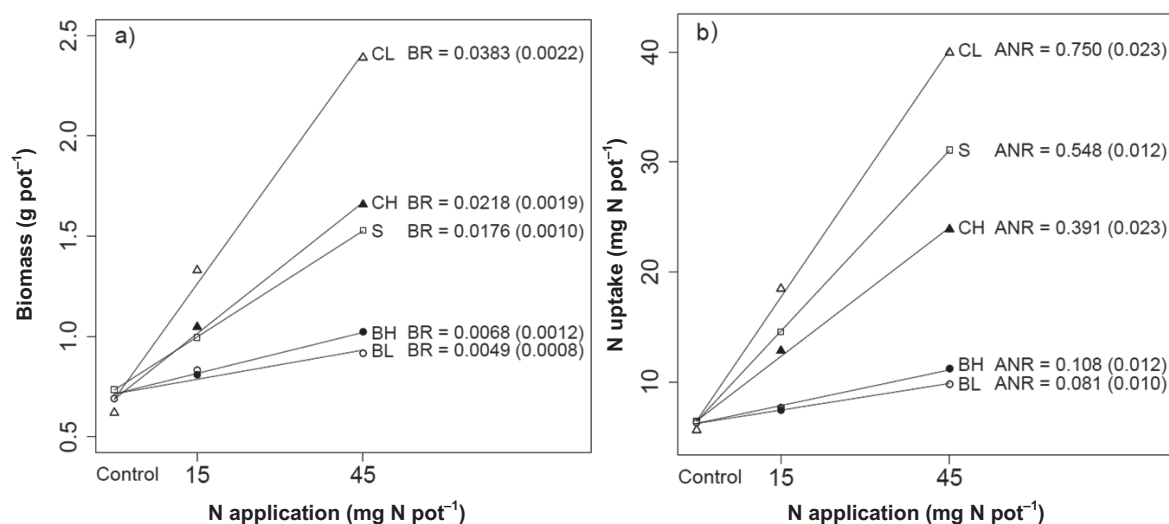
Biomass yield and N uptake were significantly lower for the control with 0.62 (± 0.05) g per pot biomass yield and 5.62 (± 0.34) mg N per pot N uptake, compared to the N-enriched materials in all ANOVA comparisons (P < 5% after Holm correction), which indicates that application of enriched biochar and clinoptilolite increased both biomass and N uptake (Fig. 2). For both biomass and N uptake, the largest means were obtained with CL45 for clinoptilolite (2.39 ± 0.09 g and 39.94 ± 0.97 mg, for biomass yield and N uptake, respectively), BH45 for biochar (1.02 ± 0.05 g and 11.23 ± 0.55 mg, for biomass yield and N uptake, respectively), and S45 for the synthetic solution treatment (1.53 ± 0.04 g and 31.09 ± 0.51 mg, for biomass yield and N uptake, respectively). Nutrient-enriched clinoptilolite at a low initial loading ratio (CL) resulted in more than a twofold increase in yield and more than a threefold increase in N uptake at 15 mg N per pot N application when compared to the control (untreated) clinoptilolite treatment (Fig. 2). The increases were even greater at 45 mg N per pot N application, with almost a fourfold and sixfold increase in yield and N uptake, respectively.

In regression models, slopes for biomass are interpreted as the biomass response (BR) and slopes for N uptake are interpreted as apparent nitrogen recovery (ANR). Among all treatments, nutrient-enriched clinoptilolite at a low initial loading ratio (CL) showed the highest BR and ANR (Fig. 3). Enriched biochar treatments (BL and BH) resulted in the lowest BR and ANR.

We investigated the effects of initial loading ratio on BR and ANR for biochar and clinoptilolite enriched at low and high initial loading ratios. Figure 3 shows that clinoptilolite enriched at a low initial loading ratio resulted in higher BR and ANR compared to clinoptilolite enriched at a high initial loading ratio (P < 0.01% for both BR and ANR). Biochar enriched at a high initial loading ratio resulted in higher BR, but the difference between the low and high initial loading ratios for biochar was not significant (P = 10%). For ANR, the difference between the low and the high initial loading ratios was small, but statistically significant (P = 3.4%).



**Figure 2:** Biomass yield and N uptake of ryegrass after 70 d of plant growth in all treatments as a result of addition of 0 (Con), 15, or 45 mg N per pot using nutrient-enriched clinoptilolite (CL: low initial loading ratio; CH: high initial loading ratio), biochar (BL: low initial loading ratio and BH: high initial loading ratio) and synthetic nitrogen (S). Error bars indicate standard errors ( $n = 4$ ).



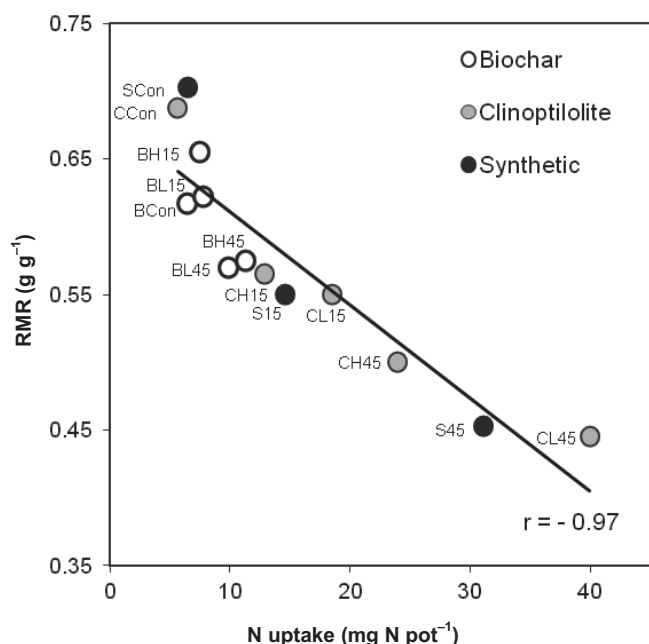
**Figure 3:** (a) Biomass response (BR) and (b) apparent N recovery (ANR) as a result of different treatments using nutrient-enriched clinoptilolite (CL: low initial loading ratio; CH: high initial loading ratio), biochar (BL: low initial loading ratio and BH: high initial loading ratio) and synthetic nitrogen (S). Standard errors in brackets ( $n = 4$ ).

We found a strong negative correlation between RMR and N uptake ( $r = -0.97$ ,  $P < 0.01\%$ ; Fig. 4). Treatments with a low N uptake resulted in a high RMR of around 0.70, while the lowest RMR was around 0.45 for both clinoptilolite enriched at a low initial loading ratio and synthetic N application. For all N-enriched biochar treatments, the mean RMR values ranged between 0.57 and 0.66, which were higher than for the treatment in which clinoptilolite was enriched at a low initial loading ratio.

## 4 Discussion

### 4.1 Effects of enriched sorbents on plant growth and N uptake

The application of enriched clinoptilolite and biochar resulted in a higher biomass yield and N uptake compared to the control treatments (Fig. 2), and this indicates that N from enriched sorbents was available to plants. Nutrient-enriched clinoptilolite resulted in up to a fourfold and sixfold increase in yield and N uptake, respectively. These findings were in line with studies that report N-loaded zeolite to be a good source of N (Ganrot et al., 2008) and urine-enriched clinoptilolite to be as effective as chemical fertilizer in preliminary pot trials (Belar-Baykal et al., 2011; Kocatürk and Baykal, 2012).



**Figure 4:** Root-to-mass ratio and N uptake of ryegrass per pot after 70 d of plant growth in all treatments as a result of different N applications at 15 and 45 mg N per pot using nutrient-enriched clinoptilolite, nutrient-enriched biochar and synthetic nitrogen; Con: control; L: low initial loading ratio; H: high initial loading ratio.

Enrichment of biochar resulted in a small, but statistically significant increase in grass biomass yield and N uptake compared to the control (untreated) biochar application (Fig. 2). *Taghizadeh-Toosi et al.* (2012a) report a two to three-fold increase in leaf dry matter yields and a twofold increase in root dry matter yields after application of  $^{15}\text{N}$ -enriched biochar when compared to treatments receiving untreated biochar. In another study, *Taghizadeh-Toosi et al.* (2012b) investigated the plant availability of N in ruminant urine-treated biochar in pot experiments with ryegrass. They found that dry matter yield was not affected, but the N uptake in plant tissues increased, indicating that the sorbed N is plant-available. In the present study, less than a twofold increase was found for both enriched biochar treatments and this means that only a small proportion of the N with which biochar had been enriched had become available to the plants. This could be due to a high retention of N by biochar which limits the availability of N to the plants through desorption. Many researchers have reported a high retention of N on the surface of biochar, even when using KCl extraction for desorption, which should replace  $\text{NH}_4^+$  ions with  $\text{K}^+$  and result in high desorption ratios. *Hina et al.* (2015) found that the amount of  $\text{NH}_4\text{-N}$  desorbed with 2 M KCl extraction from enriched biochar was only 11–18% of  $\text{NH}_4\text{-N}$ . *Sarkhot et al.* (2013) report a desorption ratio of 9–22% of  $\text{NH}_4\text{-N}$  from manure-enriched biochar with 0.001 M  $\text{CaCl}_2$  extraction, whereas *Taghizadeh-Toosi et al.* (2012b) report this ratio to be as low as 3–13% of the total N on enriched biochar with 1 M KCl extraction. *Jassal et al.* (2015) also report that only a small proportion of N (0.2–0.4 mg N  $\text{g}^{-1}$  biochar) was able to be released from N-enriched biochar with a surface concentration of 2.9–48.7 mg N  $\text{g}^{-1}$  biochar.

The difference in N availability between the clinoptilolite and biochar treatments may be attributed to the different sorption mechanisms of ammonium on biochar and clinoptilolite during enrichment, which subsequently affects the release of N from sorbents after soil incorporation. Ammonium is sorbed onto the clinoptilolite surface mainly through ion exchange and can subsequently be released slowly through desorption (*Kithome et al.*, 1998; *Hedström and Rastas Amofah*, 2008; *Belser-Baykal et al.*, 2011; *Cyrus and Reddy*, 2011; *Kocatürk and Baykal*, 2012). For biochar, some researchers report a strong relationship between cation exchange capacity and  $\text{NH}_4\text{-N}$  sorption capacity (*Hale et al.*, 2013; *Cheng et al.*, 2014; *Wang et al.*, 2015a), but other sorption mechanisms have been suggested, such as adsorption of  $\text{NH}_3$  on the biochar surface by acidic functional groups (*Taghizadeh-Toosi et al.*, 2012b), chemisorption of  $\text{NH}_3$  (*Petit et al.*, 2010), physical entrapment of  $\text{NH}_3$  in pores (*Spokas et al.*, 2012; *Jassal et al.*, 2015), and co-sorption of  $\text{NH}_4^+$  with soluble organic matter (*Sarkhot et al.*, 2013), which can cause a strong retention of N on the biochar surface. Clinoptilolite and biochar samples used in this study had different cation exchange capacities: up to 210  $\text{cmol}_c \text{ kg}^{-1}$  for clinoptilolite and 42.3  $\text{cmol}_c \text{ kg}^{-1}$  for biochar. This difference in cation exchange capacity may indicate that cation exchange plays an important role for ammonium removal by clinoptilolite. Considering the total N concentration of biochars at low (BL) and high (BH) initial loading ratios in Tab. 1, it is possible to calculate equivalents of biochars as 57.6 and 68.4  $\text{meq } 100 \text{ g}^{-1}$ , which clearly shows that other mechanisms may be involved for biochar in ammonium removal, which subsequently affects N release from sorbents when they are used as N fertilizers.

Figure 3 shows that nutrient-enriched clinoptilolite application resulted in a higher BR and ANR with clinoptilolite enriched at a low initial loading ratio (CL) compared to synthetic fertilizer application. This was a somewhat unexpected result as synthetic solution contains ammonium nitrate as an immediately available N form. Therefore, higher N availability would be expected with synthetic fertilizer as compared to the other forms of N used in this study. The reasons for this observation can only be speculated upon: it could be attributed to N losses in the synthetic fertilizer application, such as (1) nitrogen leaching from the upper pot to the lower pot during watering events and removal of that N during refreshing of the nutrient solution in the lower pot, and (2) ammonia volatilization, as some of the N in the synthetic solution is ammonium and ammonium sorption on the quartz is likely to be limited, and there is a chance that some of the ammonium has volatilized as ammonia. No tests were conducted for any losses in the synthetic N treatment. However, the relatively low ANR value of 0.55 in a N-limited system seems to indicate that losses could be substantial in the synthetic fertilizer. Clinoptilolite has been widely reported to increase plant N uptake and decrease losses of N from soil in several studies (*Ferguson and Pepper*, 1987; *Perlin et al.*, 1998; *Reháková et al.*, 2004; *Tsadilas and Argyropoulos*, 2006; *Liu and Lal*, 2015) and it may potentially prevent losses by retaining the nutrients as a slow-release fertilizer.

When selecting a sorbent, some of the most important criteria are its effectiveness to remove nutrients from digestate and

the effectiveness of the enriched sorbents, if subsequently used as a fertilizer. In a previous study, it was shown that biochar presents lower nutrient-removal efficiencies than clinoptilolite, and concentration of nutrients in oak wood biochar (same biochar as used in this study) is limited compared to clinoptilolite (Kocatürk-Schumacher et al., 2017b). The findings from the present pot experiment indicate that digestate-enriched clinoptilolite resulted in better plant growth compared to enriched biochar, which clearly indicates that clinoptilolite is superior to biochar as a nutrient-carrying sorbent. However, further research is necessary to test the effects of enriched biochar on plant growth in a long-term experiment. Another important consideration when selecting a sorbent should be its ability to function as soil improver besides its use as a nutrient carrier. In some cases renewability of the soil improver might also be important. These materials can separately or even in combination be applied in soils, depending on where they best improve soil properties and are available at low cost.

## 4.2 Effects of initial loading ratio of sorbents on plant growth and N uptake

A significant effect of initial loading ratio was found on plant growth with the enriched clinoptilolite treatments. An increase in initial loading ratio resulted in lower BR and ANR (Fig. 3). This might have been due to the different desorption behavior of clinoptilolite enriched at different initial loading ratios. Initial loading ratio influences the final amount of ammonium retained on the clinoptilolite surface, and increasing the loading ratios results in increasing ammonium concentrations (Belser Baykal et al., 2009; Kocatürk-Schumacher et al., 2017a).

In our study, the N concentration of clinoptilolite enriched at a high initial loading ratio was almost two times greater than at the low initial loading ratio (Tab. 1). Differences in desorption from clinoptilolite with different amounts of ammonium on the surface have been found previously by Dimova et al. (1999), who report a decrease of approximately 10% in the amount of ammonium desorbed from clinoptilolite, with a 30% increase in enrichment of clinoptilolite. Similarly, Hedström and Rastas Amofah (2008) reported a decrease in the release of ammonium originally transferred on zeolite surface after desorption from 0.5 mg  $\text{NH}_4\text{-N g}^{-1}$  to 0.04 mg  $\text{NH}_4\text{-N g}^{-1}$ , when the surface ammonium concentration increased by 23% (from 2.2 mg  $\text{NH}_4\text{-N g}^{-1}$  zeolite to 2.7 mg  $\text{NH}_4\text{-N g}^{-1}$  zeolite). Our results are in line with previous findings in literature, explaining different desorption behavior of clinoptilolite when it has a higher N concentration. This may also explain the limited release of N, hence, less availability to plants from clinoptilolite enriched at a higher initial loading ratio. Another explanation might be the amount of enriched sorbent being added due to different loading ratios. We assume that an increasing amount of enriched sorbents (thus, enriched at low initial loading) in the pots increases the contact with the sorbent in clinoptilolite treatments, which also makes N more available to roots. However, we have not found any studies in the literature to support this; therefore, this topic needs further research.

For biochar, the effect of initial loading ratio was statistically significant only for ANR. Contrary to clinoptilolite, increasing

the initial loading ratio resulted in higher ANR, which may indicate that more N was released from biochar enriched at a high initial loading ratio. As discussed earlier, in literature, biochar has been reported to strongly retain  $\text{NH}_4\text{-N}$ , which allows biochar to release only a small proportion of N from the biochar surface. Even so, the desorption behavior of biochar was found to be different in literature with different amounts of N transferred onto the biochar surface and a higher desorption from the biochar surface with an increasing N concentration in biochar (Sarkhot et al., 2013; Hina et al., 2015) and, therefore, an increasing initial loading ratio.

Initial loading ratio is an important factor when designing a system to remove nutrients by sorption processes since it affects the removal efficiency and amount of nutrients sorbed by sorbents (Belser Baykal et al., 2009; Kocatürk-Schumacher et al., 2017a, 2017b). Our results show that initial loading ratio is an important factor when the enriched sorbents are to be used as a fertilizer, since it affects the availability of N.

## 4.3 Root-to mass ratio (RMR)

A higher biomass allocation to the roots than to the leaves can be observed under low and limiting N levels (Wilson, 1988; Poorter and Nagel, 2000) and, therefore, a lower root-to-total biomass ratio indicates increasing nitrogen availability (Pérez-Harguindeguy et al., 2013). The data presented in Fig. 4 show that a strong negative correlation ( $r = -0.97$ ,  $P < 0.01\%$ ) was also found between RMR and N uptake. Clinoptilolite enriched at a low initial loading ratio (CL45) and synthetic (S45) treatment resulted in a similarly low RMR. This observation supports our findings discussed above that both treatments led to similar N availability although they resulted in different N uptake. In contrast to nutrient-enriched clinoptilolite, enriched biochar resulted in a high RMR as a result of invariably low N availability in all N application levels.

## 5 Conclusions

We found that both enriched biochar and clinoptilolite were able to increase biomass yield and N uptake, but clinoptilolite resulted in much higher biomass response and apparent N recovery compared to enriched biochar. However, further research in a long-term experiment and field experiments are crucial to test the effects of enriched sorbents on plant growth. We also found that initial loading ratio is an important parameter that not only affects the nutrient removal efficiency from the liquid fraction of digestate, but also affects the availability of N and thereby the efficiency of the enriched material when used as a fertilizer. This information is important if the enriched material is to be applied on soil as a fertilizer.

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